

## PATENT COOPERATION TREATY

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REC'D 25 JAN 2005

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INTERNATIONAL PRELIMINARY EXAMINATION REPORT  
(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 62198A	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US 03/30632	International filing date (day/month/year) 26.09.2003	Priority date (day/month/year) 24.10.2002
International Patent Classification (IPC) or both national classification and IPC C07C7/12		
Applicant DOW GLOBAL TECHNOLOGIES INC. et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
 

This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.
3. This report contains indications relating to the following items:
  - I  Basis of the opinion
  - II  Priority
  - III  Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
  - IV  Lack of unity of invention
  - V  Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
  - VI  Certain documents cited
  - VII  Certain defects in the international application
  - VIII  Certain observations on the international application

Date of submission of the demand 06.05.2004	Date of completion of this report 24.01.2005
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized Officer  Cooper, S Telephone No. +49 89 2399-8323



# INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/US 03/30632

## I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

### Description, Pages

1-25 as originally filed

### Claims, Numbers

1-33 received on 06.12.2004 with letter of 06.12.2004

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

5.  This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).  
*(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)*

6. Additional observations, if necessary:

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**IV. Lack of unity of invention**

1. In response to the invitation to restrict or pay additional fees, the applicant has:
  - restricted the claims.
  - paid additional fees.
  - paid additional fees under protest.
  - neither restricted nor paid additional fees.
2.  This Authority found that the requirement of unity of invention is not complied with and chose, according to Rule 68.1, not to invite the applicant to restrict or pay additional fees.
3. This Authority considers that the requirement of unity of invention in accordance with Rules 13.1, 13.2 and 13.3 is
  - complied with.
  - not complied with for the following reasons:  
**see separate sheet**
4. Consequently, the following parts of the international application were the subject of international preliminary examination in establishing this report:
  - all parts.
  - the parts relating to claims Nos. 1-11(partially),12-15,20(partially),21-29 .

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes: Claims	
	No: Claims	1-11(partially),12-15,20(partially),21-29
Inventive step (IS)	Yes: Claims	
	No: Claims	1-11(partially),12-15,20(partially),21-29
Industrial applicability (IA)	Yes: Claims	1-11(partially),12-15,20(partially),21-29
	No: Claims	

**2. Citations and explanations**

**see separate sheet**

**Section III.**

1). The following two inventions were identified in the present application:

i) Claims 1-11 (partially), 12-15, 20 (partially), 21-29.

A process for stabilising an olefinic mixture produced by metathesis of olefins in the presence of a metallic metathesis catalyst in which metals are removed by contact with an adsorbent (claims 1-11 partially, 12-15, 20 partially and 27-29) and an olefin composition produced by such a process having a specified concentration of metals (claims 21-26).

ii) Claims 1-11 (partially), 16-19, 20 (partially), 30-33.

A process for stabilising an olefinic mixture produced by metathesis of olefins in the presence of a metallic metathesis catalyst in which metals are removed by distillation.

2). Processes for stabilising an olefinic mixture produced by metathesis of olefins in the presence of a metallic metathesis catalyst in which the stabilisation involves removing the metals are known from all three non-patent documents cited on p.3 of the application. Tetrahedron Letters vol.40, pp.4137-4140, (1999) is cited as representative with particular reference being made to the last two sentences of the first full paragraph on p.4137. The present application is therefore characterised by the method with which the metals are removed. In this respect no common technical features can be seen linking the two methods claimed viz. contact of the metathesis product with an adsorbent and distillation.

**Section V.**

D1 = JP-A-3066725

D2 = US-A-5 539 060

D4 = Tetrahedron Letters (1999), 40, 4137-4140

D6 = DE-A-100 41 345

1). According to entries 1-3 and 5-7 of the table on p.210 of D1 W and Al metathesis catalysts have been removed from an olefin metathesis product to a level of less than 30 ppm by treating it with adsorbents. Claim 21 therefore lacks novelty.

**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

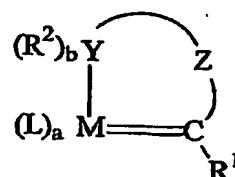
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- 2). Since it is known from all three non-patent literature documents cited on p.3 of the present application with the last two sentences of the first full paragraph on p.4137 of D4 being cited as representative that the olefin products of olefin metatheses are stabilised by the removal of the metal metathesis catalysts; claim 1 is also lacking novelty over the disclosure of D1.
- 3). Concerning the novelty of claims 1 and 21, the applicant will be expected to confirm that the process conditions employed in comparative example 2 of D2 do not give rise to an olefin metathesis product having less than 30 ppm metal catalyst residues.
- 4). Concerning the novelty of claim 21, the applicant will be expected to confirm that **none** of the olefin streams arising in the course of the example of D6 give rise to a product containing less than 30 ppm of the metathesis catalyst metals.

WHAT IS CLAIMED IS:

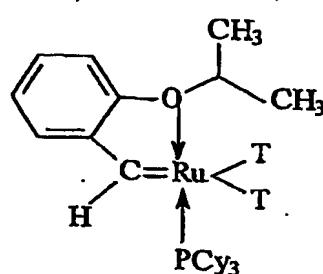
1. A method of stabilizing an olefin metathesis product mixture comprising (a) contacting an olefin metathesis product mixture comprising one or more olefins obtained in a metathesis process, a metathesis catalyst comprising a catalytic metal, optionally, one or more metathesis catalyst degradation products, and optionally, one or more metals derived from sources other than the catalyst and catalyst degradation products, with an adsorbent; or (b) subjecting the olefin metathesis product mixture to a first distillation to remove substantially volatiles and lights, and thereafter, subjecting bottoms from the first distillation to a second distillation in a wiped film evaporator; the (a) adsorbent or (b) distillation method being conducted under conditions sufficient to remove metal(s) to a concentration less than about 30 parts per million by weight.
2. The method of Claim 1 wherein the olefin metathesis product mixture comprises a C<sub>2-20</sub> substituted or unsubstituted olefin or a mixture thereof.
3. The method of Claim 2 wherein the C<sub>2-20</sub> substituted or unsubstituted olefin is a monoolefin or a polyolefin.
4. The method of Claim 1 wherein the olefin metathesis product mixture comprises a C<sub>2-20</sub>  $\alpha$ -olefin, a C<sub>2-20</sub>  $\alpha, \omega$ -unsaturated acid, a C<sub>2-20</sub>  $\alpha, \omega$ -unsaturated ester, or a combination thereof.
5. The process of Claim 1 wherein the catalytic metal is selected from ruthenium, tungsten, molybdenum, rhenium, or a combination thereof.
6. The process of Claim 1 wherein the metathesis catalyst is selected from the group consisting of dichloro-3,3-diphenylvinylcarbene-bis(tricyclohexylphosphine)-ruthenium (II), bis(tricyclohexylphosphine)benzylidene ruthenium dichloride, bis(tricyclohexylphosphine)benzylidene ruthenium dibromide, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium dibromide, and tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium diiodide.
7. The process of Claim 1 wherein the metathesis catalyst is selected from dichloro-3,3-diphenylvinylcarbene-bis(tricyclohexylphosphine)-ruthenium (II), bis(tricyclohexylphosphine)benzylidene ruthenium dichloride,

tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]{benzylidene}ruthenium (IV) dichloride, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]{benzylidene}ruthenium (IV) dibromide, tricyclohexylphosphine[1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene]{benzylidene}ruthenium (IV) diiodide, and chelated ruthenium complexes represented by the following formula:



wherein M is Ru; each L is independently selected from neutral and anionic ligands in any combination that balances the bonding and charge requirements of M; a is an integer, preferably from 1 to about 4, which represents the total number of ligands L; R<sup>1</sup> is selected from hydrogen, straight-chain or branched alkyl, cycloalkyl, aryl, and substituted aryl radicals; Y is an electron donor group of an element from Group 15 or 16 of the Periodic Table; each R<sup>2</sup> is independently selected from hydrogen, alkyl, cycloalkyl, aryl, and substituted aryl radicals sufficient to satisfy the valency of Y; b is an integer, preferably 0 to about 2, representing the total number of R<sup>2</sup> radicals; and Z is an organic diradical that is bonded to both Y and the carbene carbon (C) so as to form a bidentate ligand, which ligand in connection with the M atom forms a ring of from about 4 to about 8 atoms.

8. The process of Claim 1 wherein the metathesis catalyst is...



wherein each T is independently selected from Cl and Br, and  $^3\text{PCy}_3$  is tricyclohexylphosphine.

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9. The process of Claim 1 wherein the metathesis catalyst is supported on a catalyst support.
10. The process of Claim 1 wherein metals other than those derived from the catalyst and catalyst degradation products are present and the metals are selected from iron, nickel, copper, zinc, cobalt, chromium, lithium, sodium, potassium, magnesium, calcium, and mixtures thereof.
11. The process of Claim 1 wherein the catalyst degradation product is derived from the reaction of the ligand with oxygen or water.
12. The process of Claim 1 wherein the olefin metathesis product mixture is contacted with an adsorbent.
13. The process of Claim 12 wherein the adsorbent is selected from carbon, clays, reticular cross-linked ion-exchange resins, alumina, silica-alumina, and mixtures thereof.
14. The process of Claim 13 wherein the adsorbent is a wood carbon.
15. The process of Claim 12 wherein the contacting with adsorbent is effected at a temperature greater than about -5°C and less than about 50°C.
16. The process of Claim 1 wherein the olefin metathesis product mixture is subjected to distillation as in (b) to remove metal(s) to a concentration of less than about 100 ppb.
17. The process of Claim 16 wherein the first distillation to remove lights and volatiles is operated at a temperature greater than about 40°C and less than about 150°C and a pressure greater than about 15 mm Hg (20 kPa) and less than about 100 mm Hg (132 kPa).
18. The process of Claim 16 wherein the second distillation is conducted in a short path wiped-film evaporator that is operated at a temperature greater than about 150°C and less than about 200°C.
19. The process of Claim 16 wherein the second distillation is conducted in a short path wiped-film evaporator that is operated at a pressure greater than about 0.001 mm Hg (1.3 Pa) and less than about 5 mm Hg (6.6 kPa).
20. The process of Claim 1 wherein the concentration of metal(s) after stabilization is less than about 1 ppm by weight.
21. A stabilized olefin metathesis product composition comprising one or more olefins produced in a metathesis process and having a total concentration of

metals of less than about 30 parts per million by weight, based on the weight of the olefin metathesis product mixture.

22. The stabilized olefin metathesis product composition of Claim 21 wherein the product olefin is selected from the group consisting of  $C_{2-20}\alpha$ -olefins,  $C_{2-20}\alpha,\omega$ -unsaturated esters,  $C_{2-20}\alpha,\omega$ -unsaturated acids, and combinations thereof.

23. The composition of Claim 21 further comprising one or more metathesis catalyst ligands, metathesis catalyst degradation products, or a combination thereof.

24. The composition of Claim 21 further comprising a solvent.

25. The composition of Claim 21 further comprising a stabilizing ligand.

26. The composition of Claim 21 further comprising one or more unconverted reactant olefins.

27. A method of removing metal(s) from an olefin metathesis product mixture comprising contacting a mixture comprising one or more olefins obtained in a metathesis process and one or more catalytic and/or non-catalytic metals with an adsorbent under conditions sufficient to reduce the total metal concentration to less than about 30 parts per million by weight, based on the weight of the olefin metathesis product mixture.

28. The method of Claim 27 wherein the adsorbent is selected from the group consisting of carbon, diatomaceous earth, clays, silica gel, reticular cross-linked ion-exchange resins, alumina, silica-alumina, and combinations thereof.

29. The method of Claim 27 wherein the adsorbent is a wood carbon.

30. A method of removing metal(s) from an olefin metathesis product mixture comprising subjecting a product mixture comprising one or more olefins obtained in a metathesis process and one or more catalytic and/or non-catalytic metals to a first distillation under conditions sufficient to remove substantially volatiles and lights, and thereafter, subjecting bottoms from the first distillation to short path wiped-film evaporation under conditions sufficient to reduce the total metal concentration in the olefin product mixture to less than about 30 parts per million by weight, based on the weight of the olefin metathesis product mixture.

31. The method of Claim 30 wherein the temperature of the short path wiped-film evaporation is greater than about 150°C and less than about 200°C.

32. The method of Claim 30 wherein the pressure in the short path wiped-film evaporator is greater than about 0.001 mm Hg (1.3 Pa) and less than about 5 mm Hg (6.6 kPa).

33. The method of Claim 27 or 30 wherein the olefin metathesis product mixture comprises 1-décene, methyl decenoate, and methyl oleate.